

TOPIC 16 – KINETICS

16.2 – REACTION MECHANISM

IB Chemistry
T16D07



16.2 Reaction mechanism (1 hour)

- 16.2.1 Explain that reactions can occur by more than one step and that the slowest step determines the rate of reaction (rate-determining step). (3)
- 16.2.2 Describe the relationship between reaction mechanism, order of reaction and rate-determining step. (2)



16.2 – Reaction Mechanism

- Most reactions that occur at a measureable rate occur as a series of simple steps
- The sequence of steps is known as the **reaction mechanism**
- The individual steps, **elementary steps**, usually cannot be observed directly so this is in fact a theory about the sequence of events
- Kinetic evidence can support a particular mechanism but it cannot prove it to be correct



16.2 - Intermediates

- Often the products of a single step are used in the next step and therefore only appear as **intermediates**, not as final products
- The sum of the individual steps must be equal to the overall equation (intermediates cancel out)



16.2 – Intermediate Example

- $\text{NO}_2(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$
 - Step 1: $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{NO}_3(\text{g})$
 - Step 2: $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$
 - NO_3 is an intermediate, it is being produced and consumed, same with the extra NO_2



16.2 – Intermediate Example 2

- $2\text{HI}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
 - Step 1: $\text{I}^-(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{IO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 - Step 2: $\text{H}^+(\text{aq}) + \text{IO}^-(\text{aq}) \rightarrow \text{HIO}(\text{aq})$
 - Step 3: $\text{I}^-(\text{aq}) + \text{HIO}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + \text{OH}^-(\text{aq})$
 - Step 4: $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$



16.2 - Molecularity

- The **molecularity** is used in reference to an elementary step to indicate the number of reactant species involved.
 - **Unimolecular Reaction:** elementary reaction that involves a single reactant particle ($A \rightarrow B$)
 - **Bimolecular Reaction:** involves two reactant particles ($A + B \rightarrow C$)
 - In the last slide, the reaction between NO_2 and CO , both elementary steps are bimolecular
 - **Termolecular Reactions:** because of collision theory and low probability of >2 particles colliding (same time, E_a , orientation) = RARE



16.2 – Rate-determining Step

- The products of the reaction appear only as fast as the products of the **rate-determining** elementary step.
- The rate-determining step determines the overall rate of reaction
- Think of traffic in an overcrowded city. If the highway is 4 lanes in each direction and the bridge to get over the river is only a single lane in each direction due to construction. The number of cars that can cross the bridge in a given amount of time determines the rate of traffic



16.2 – Rate-determining Step

- Because the rate determining step is an elementary step (a single molecular event) its rate law comes directly from its molecularity
- Per collision theory, the [reactant] in the rate-determining step must appear in the rate law for that step, raised the power of its coefficient
 - With regard to using the stoichiometric coefficient. This **ONLY** applies for **ELEMENTARY STEPS** and remember this assumption cannot be made for the rate expression of the overall reaction



16.2 – Rate Law from

- The rate law for the rate-determining step, predictable from its equation, leads us to the rate expression for the overall equation.
- If the rate-determining step is the first step or the only step in the mechanism, then its rate law is the same as the expression for the overall reaction

Equation for rate-determining step	Molecularity	Rate Law
$A \rightarrow \text{Products}$	Unimolecular	$\text{Rate} = k[A]$
$2A \rightarrow \text{products}$	Bimolecular	$\text{Rate} = k[A]^2$
$A + B \rightarrow \text{products}$	Bimolecular	$\text{Rate} = k[A][B]$

16.2 – Rate Law for Elementary

- When the rate-determining step is the first step
- $2\text{NO}_2\text{Cl}(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \text{Cl}_2(\text{g})$
 - Step 1: $\text{NO}_2\text{Cl}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{Cl}(\text{g})$
 - This step is slow: rate-determining step
 - Step 2: $\text{NO}_2\text{Cl}(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{Cl}_2(\text{g})$
 - This step is fast
 - Rate = $k[\text{NO}_2\text{Cl}]$ first order reaction



16.2 – Rate Law for Elementary

- When the rate-determining step is not the first step in the mechanism, the situation is a bit more complicated because the [reactant] depend on an earlier step which must be taken into account:
- $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
 - Step 1: $\text{NO}(\text{g}) + \text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}_2(\text{g})$
 - fast
 - Step 2: $\text{N}_2\text{O}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
 - Slow: rate-determining step
- Rate = $k[\text{N}_2\text{O}_2][\text{O}_2]$ (but N_2O_2 depends on $[\text{NO}]^2$)
- Rate = $k[\text{NO}]^2[\text{O}_2]$ (third order overall reaction)



16.2 – Rate Expression Explained

- These examples explain why the order of the reaction with respect to each reactant is not linked to their coefficients in the overall equation for the reaction but instead determined by the coefficients in the rate-determining elementary step!
- **Zero Order Explanation:**
 - [reactant] does not affect the overall rate because it does not take part in the rate determining step
 - If a reactant does appear in the rate expression step (1st or 2nd order), then it, or a derivative of it, must appear in the rate-determining step



16.2 – Transition State Theory

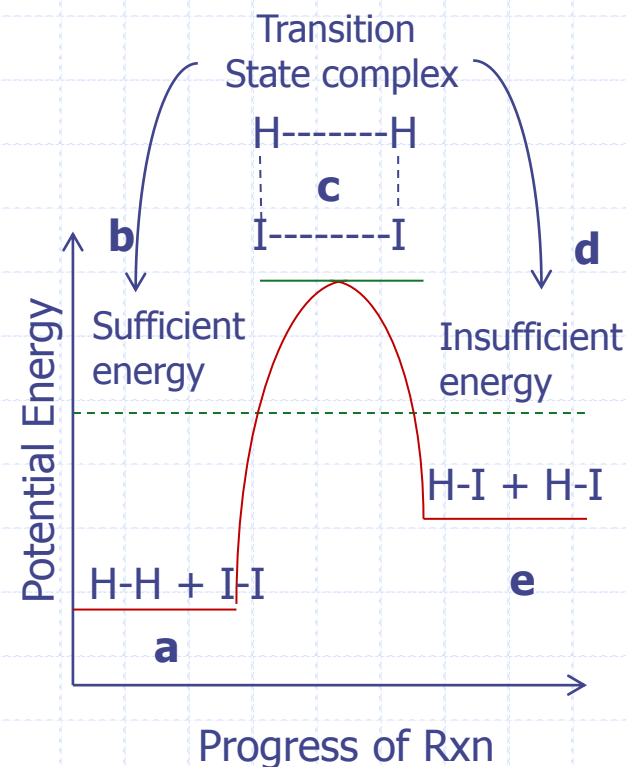
- The **transition-state theory** suggests that as molecules collide and bond breaking/formation take place, the interacting molecules are temporarily in a high-energy and unstable state.
 - This state is known as a **transition state** or **activated complex**
 - This state has a higher enthalpy or PE than either reactants or products and is unstable
 - State can decompose to re-form reactants or it can undergo further changes to form products



16.2 – Transition State Theory

- For example, the simple bimolecular reaction between $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ to form $\text{HI}(\text{g})$

- Enthalpy of individual I_2 and H_2
- Weak covalent bonds begin to form between H and I, at the same time H-H and I-I bonds begin to weaken
- Formation of transition state or activated complex
- H-I bonds continue to shorten and strengthen, H-H and I-I continue to weaken
- Formation of 2HI molecules and their enthalpy



16.2 – Transition State Theory

- HI is only formed if the colliding H_2 and I_2 have
 - Sufficient energy to overcome E_a barrier
 - H_2 and I_2 must collide in a sideways fashion, this is the steric factor or collision geometry
- The TST (transition state theory in short) can be used to calculate reaction rates and transition states from a knowledge of:
 - Molecular structures
 - Shapes of reactants

